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(54) Title: POLYESTER RESIN COMPOSITION AND RESIN PRODUCT FOR CALENDERING.

(57) Abstract: A polyester resin composition for calendering which comprises a polyester resin and a metal salt of an organic phosphate as a lubricant; the polyester resin composition which further comprises an organic phosphate and/or a polyolefin wax as a lubricant; the polyester resin composition which further comprises an antioxidant in addition to the above lubricant. The polyester resin composition exhibits extremely good roll releasability in calendering and thus the use thereof allows the production of a sheet with no troubles in practical production (long run commercial production). Moreover, the resultant sheet is greatly improved in transparency and the resistance to thermal discoloration as compared to a conventional polyester resin sheet of this type.

Attached document: International Search Report
As for two-letter codes and other abbreviations, one must refer to "Guidance Note for Codes and Abbreviations".

Detailed description

POLYESTER RESIN COMPOSITION AND RESIN PRODUCT FOR CALENDERING

Technological field

This invention is concerned with the technological field of calendar fabrication of polyester resins. This invention offers a polyester resin product to be fabricated into sheets with the characteristics that the resin has an excellent property of being separated from the roll and of being fabricated into sheets with high transparency.

Background technology

In the past, extrusion fabrication has been used in the production of sheets or films made from polyester resins, because of the ease of fabrication. However, with extrusion fabrication, the friction between the resin and the dye lip affects the fabrication property of the polyester resin, so that the accuracy is poor with regard to the thickness and width of the sheets (films) as well as the direction of flow, so that the method is not adequate for mass production. For this

reason, the desire has been keen for a polyester resin with which it is possible to produce a sheet (film) by the process of calendar fabrication adequate for mass production. However, it has been difficult to apply calendar fabrication to polyester resins for general use, represented by polyethylene terephthalate (PET), because of its crystalline property. Also the resin tends to adhere to the roll because of its strong adhesiveness after the thermal plasticizing process. Because of such a situation, resin products for calendar fabrication have been proposed: a resin product of a copolymerized polyester resin produced by the copolymerization of polyethylene terephthalate and 1,4-cyclohexanedimethanol, added with a gliding agent (U.S. Patent 6,068,910; Japanese Kokai Patent Nos. Hei 11[1999]-343353 and 2000-186191). In these products, the fabrication property was improved by a reduction of the crystalline property of the polyester through the co-polymerization of 1,4-cyclohexanedimethanol and of the adhesiveness of the resin to the roll after the thermal plasticizing process by a gliding agent, such as fatty acid esters, organophosphate esters, metal soaps with higher fatty acids, gliding agent of the fatty acid amide type, polyethylene wax, and paraffin wax.

However, when we examined the calender fabrication property of a polyester resin obtained by the co-polymerization of 1,4-cyclohexanedimethanol, the melt viscosity was high at the calender temperature presumably due to the rigid nature of the cyclohexane ring. Therefore, kneading was necessary in calendering at a relatively high temperature and the material tended to adhere to the roll. While it was possible to carry out calender fabrication in a relatively short time by the incorporation of the gliding agent, when mixing and kneading were carried out for a long time, the material tended to adhere to the roll, making it impossible to carry out a stable calender fabrication. In the case of calender fabrication (batch type calendering) in actual industrial production, the resin used as the source material and the gliding agent used as the additive are mixed in a blender such as a Banbury mixer or mixing roll, followed by introduction onto the calender roll. It requires 15-30 minutes for the final mixture to be led from the mixer to the calender roll. The adhesiveness to the roll was not sufficiently improved in the mixture, which had been mixed for such a long time. Also, if the production line is stopped for some reason, the mixture remains on the roll; when this happens, it requires much labor and a long time to remove the mixture from the roll.

The aforementioned report described the transparency of the sheet obtained by calender fabrication carried out on the polyester resin copolymerized with 1,4-cyclohexanedimethanol. The haze value of this is 30-40% at most and it is not appropriate to be used as the sheet for which a high transparency is required, such as that used as sheets for building materials, sheets for food containers, and sheets for blister packs. When a large amount of gliding agent is used in kneading for a long time, the transparency of the sheet is reduced, resulting in the impossibility of obtaining products with high transparency by calendering fabrication in industrial production.

The printing characteristic is worsened in the sheet obtained after the use of a large amount of gliding agent due to mixing and kneading for a long time; furthermore, there is the problem that the sheet becomes tainted after exposure to high temperature, if the gliding agent proposed in the aforementioned publication is used as the main agent.

General description of the invention

The aim of this invention is to offer a polyester resin product for calender fabrication with the following characteristics: with the background described above, a highly transparent sheet with the excellent property of being removed from roll can be produced in actual production (long-running fabrication in industrial production).

Also, the aim of the invention is to offer a polyester resin product, for calender fabrication, from which it is possible to produce sheets with high transparency and having the excellent characteristic of being tinted with high resistance to heat.

Another aim of the invention is to offer a polyester resin for calendar fabrication with the following characteristics: excellent mutual solubility with a lubricant, so that an excellent roll-removal characteristic is obtained, improved transparency of the sheet, and excellent mechanical properties such as extension and strength following fabrication.

Another aim is to offer sheets with the characteristics of high transparency and coloration with high resistance to heat, thus far not achieved.

Another aim is to offer a sheet with high transparency that has thus far been impossible to obtain, along with excellent resistance to color fading induced by heat. We strived to achieve the aims described above and discovered that a marked improvement can be obtained with respect to removal from the roll in the calendar fabrication process by incorporating a metal organophosphate ester as the lubricant with a polyester resin, with the further benefit of a marked improvement in the properties of sheet after fabrication. The invention is the result of this discovery.

The invention offers the following:

(1) Polyester resin product for calendar fabrication, characterized by a certain content of polyester resin and metal organophosphate ester.

(2) Polyester resin product for calendar fabrication described in the aforementioned (1), in which the metal organophosphate ester is a metal phosphate monoester or phosphate diester.

(3) Polyester resin product for calendar fabrication described in the aforementioned (2), in which the phosphate monoester and phosphate diester are esters of polyether alcohols.

(4) Polyester resin product for calendar fabrication described in the aforementioned (1), in which the metal organophosphate ester is a metal organophosphate ester represented by general formula (I) and/or is a metal organophosphate ester represented by general formula (II).

Formula (I):

$$[[RO(C_fH_{2f}O)_n]_{3-a-e}PO(O)_a(OH)_e]_d[M(OH)_b]_c,$$

where R represents a hydrocarbon group with 4-30 carbon atoms; M indicates an alkali metal or alkaline earth metal, Zn, or Al; a indicates 1 or 2; e indicates 0 or 1 (e is 0 or 1 when a is 1 and 0 when a is 2); b indicates 0-2; c indicates 1 or 2; d indicates 1-3; f indicates 2 or 3; n indicates 0-60; and a, b, c, and d have the following relation with the valence of metal (M) (represented by m, hereafter): when m=1, b=0, d=1, a=c; when m=2, b=0, c=1, axd=2 or b=1, d=1, a=c; when m=3, b=0, d=3, a=c, b=1, c=1, axd=2 or b=2, d=1, a=c; furthermore, when $m \geq 2$, the metal (M) can be combined with phosphate ions, mutually different, and in this case, d=2 or 3 indicates the total number of mutually different phosphate ions. When d=2 or 3, the structure within the sign [ ] could be identical or different.

Formula (II):

$$[[R^1O(C_fH_{2f}O)_n]_{3-a-e}PO(O)_a(OH)_e]_d[M(OCOR^2)_s(OH)_x]_t$$

where R^1 indicates a hydrocarbon group containing 4-30 carbon atoms; R^2 indicates an alkyl group containing 1-25 carbon atoms; M indicates an alkali metal or alkaline earth metal, Zn, or Al; a indicates 1 or 2; e indicates 0 or 1 (e is 0 or 1 when a is 1 and 0 when a is 2); d indicates 1 or 2; s indicates 1 or 2; x indicates 0 or 1; t indicates 1 or 2; f indicates 2 or 3; and n indicates 0 to 60. Also, s+x=1 or 2. The following relation exists among a, d, s, t and the valence (designated as m, hereafter) of the metal (M): when m=2: s=1, d=1, and a=t; when m=3: s=1, t=1, axd=2 or s=2, d=1, a=t, and when m=3, mutually different phosphate ions could be bound to the metal (M) and in that case, d=2 indicates the sum of the number of various phosphate ion groups. When d=2. the structures within [ ] can be identical or different.

(5) Polyester resin product for calendar fabrication described in any of the aforementioned sections (1)-(4) in which the polyester resin is characterized as follows: the polyester resin contains a terephthalic acid component at 50 mol% or more with respect to the total dicarboxylic acid component and an ethylene glycol component at 50 mol% or more with respect to the total diol component, and the polyester resin contains isophthalic acid at 5-50 mol% with respect to the total dicarboxylic acid component and/or at least one type of diol component chosen from the group of 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, neopentyl glycol, diethylene glycol, and 1,4-cyclohexanedimethanol at 5-50 mol%.

(6) Polyester resin product for calendar fabrication described in Claim (5), in which the polyester resin contains a neopentyl glycol component, at the least.

(7) Polyester resin product for calendar fabrication described in the aforementioned (1) - (6), characterized by a certain content of a polyolefin wax.

(8) Polyester resin product for calendar fabrication described in any of Claims (1) - (7), characterized by a certain content of an organophosphate ester.

(9) Polyester resin product for calendar fabrication described in any of Claims (1) - (8), characterized by a certain content of antioxidant.

(10) Polyester resin product for calendar fabrication containing a polyester resin and lubricant, characterized by the time for adhesion to the heated roll at 180°C being 15 min or more.

(11) Polyester resin product containing a polyester resin and lubricant for calendar fabrication, characterized by the adhesion time being 15 minutes or more to the heated roll at 180°C and the haze being 20% or less when the product is made into a 0.7-mm-thick sheet.

(12) Polyester resin product for calendar fabrication with the following characteristics: the product contains a terephthalic acid component at 50 mol% or more with respect to the total dicarboxylic acid component and an ethylene glycol component at 50 mol% or more with respect to the total diol component, and/or at least one diol component chosen from the group of 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, neopentyl glycol, and diethylene glycol at 5-50 mol%.

(13) Polyester resin product for calendar fabrication described in (12), with the characteristics of the glass transition temperature being 40-90°C and the softening temperature being 130-210°C.

(14) Sheet obtained by calendar fabrication carried out on the polyester resin product described in any of the aforementioned Claims (1)-(11).

Best form in which this invention is realized

The polyester resin product of this invention for calendar fabrication (abbreviated as polyester resin product or resin product, hereafter) is characterized by the incorporation of a metal organophosphate ester, at the least, in the polyester resin.

The metal organophosphate ester used in this invention is described as follows: a phosphate monoester in which at least one hydrogen ion is replaced with a metal ion in 2 hydroxy groups not reacting with an alcohol (the metal ion could be further bonded with a hydroxy or acyloxy group). Among them, preferable are ester compounds obtained by the esterification of a phosphate monoester or diester [sic] with a polyether alcohol source substance (in other words, an ester of a polyether alcohol).

Especially preferable are metal organophosphate esters represented by general formula (I) or (II) below.

formula (I):

$$[[RO(C_fH_{2f}O)_n]_{3-a-e}PO(O)_a(OH)_e]_d[M(OH)_b]_c$$

[where R indicates a hydrocarbon group containing 4-30 carbon atoms; M indicates an alkali metal, alkaline earth metal, Zn, or Al; a indicates 1 or 2; e indicates 0 or 1 (e is 0 or 1 when a=1 and is 0 when a=2); b indicates 0-2; c indicates 1 or 2; d indicates 1-3; f indicates 2 or 3; n indicates 0-60; a, b, c, and d have the following relations with the valence (designated as m) of

metal (M), when m=1, b=0, d=1, a=c; when m=2, b=0, c=1, axd=2, or b=1, d=1, a=c; when m=3, b=0, d=3, a=c, b=1, c=1, axd=2 or b=2, d=1, a=c. Furthermore, when $m \geq 2$, mutually different phosphate ion groups can be combined with metal (M), and in this case d=2 or 3 indicates the sum of mutually different phosphate ion groups. Also, when d=2 or 3, the structures within [ ] could be identical or different.

formula (II):

$$[[R^1O(C_fH_{2f}O)_n]_{3-a-e}PO(O)_a(OH)_e]_d[M(OCOR^2)_s(OH)_x]_t$$

where R^1 indicates a hydrocarbon group of 4-30 carbon atoms; R^2 indicates an alkyl group of 1-25 carbon atoms; M indicates an alkali metal, alkaline earth metal, Zn or Al; a indicates 1 or 2; e indicates 0 or 1 (under the stipulation that e is 0 or 1 when a is 1 and is 0 when a is 2); d indicates 1 or 2; s indicates 1 or 2; x indicates 0 or 1; t indicates 1 or 2; f indicates 2 or 3; n indicates 0-60, s+x=1 or 2, and as for a, d, s, and t, there are the following relations with the valence (m) of metal (M): if m=2, s=1, d=1 and a=t; if m=3, s=1, t=1, axd=2 or s=2, d=1, a=t; further, if m=3, different phosphate ions can be bound to metal (M), and in this case d=2 indicates the total number of various types of phosphate ion groups. Also, when d is 2, the structures within [ ] can be the same or different.

As a hydrocarbon group containing 4-30 carbon atoms represented by R in general formula (I) and hydrocarbon group containing 4-30 carbon atoms represented by R^1 in general formula (II), preferable are an alkyl group, phenyl group, arylalkyl group, alkenyl group, and alkylphenyl group. As the alkali metal represented by M in general formula (I) and general formula (II), one can cite Li, Na, and K. As the alkaline earth metal, one can cite Mg, Ca, and Ba.

One can produce metal organophosphate esters by conventional methods, and the method is not restricted to those of (I) and (II).

As preferable examples of metal organophosphate esters of general formula (I), one can cite compound (1) to compound (13) in Table 1 below and compound (14) to compound (16) in Table 2 below. As preferable examples of metal organophosphate esters represented by general formula (II), one can cite compound (17) to compound (26) in Table 2 below.

With these compounds (compound (1) to compound (26)), the repeating number is represented by a decimal number for oxyethylene or oxytrimethylene in a polyether alcohol component (repeating number (n) in formula $(C_fH_{2f}O)_n$). This is because of the fact that the repeating number for oxyethylene or oxytrimentylene in the polyether alcohol represents those of several phosphate esters with the same or different repeating number used in a single mixture or product.

It is possible to use one or two types of compounds represented by general formula (I) or (II) (metal organophosphate ester). In other words, the following methods are allowed: use is

made of one type or use is made of two types or more of compounds represented by general formula (I) (compounds represented by general formula (II) are not used); or use is made of one or two compounds represented by general formula (I) and one or two compounds represented by general formula (II), or use is made of one, two, or more types of compounds represented by general formula (II) (the compound represented by general formula (I) is not used).